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by

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16. ABSTRACT

Dry deposition contributes significantly to the acidification of the ecosystem. However, difficulties in measuring dry deposition of reactive gases and fine particles make routine direct monitoring impractical. An alternate approach is to use the "concentration monitoring" method in which dry deposition is estimated from the product of measured concentration and estimated deposition velocity. To investigate sampling protocols for estimating the weekly averages of pollutant dry deposition, a sampler that performs over the period of about 0.25 to 7 days, depending on atmospheric concentrations has been developed. It consists of a Teflon cyclone to exclude particles larger than aout 2 μm, selective solid adsorption media for reactive gases - some of which are sampled from an unstable transition flow to avoid bias from particle evaporation, and a particle filter. The sampler is the first reported application of unstable transition-flow mass transfer for the collection of trace atmospheric gases. Laboratory and limited field tests have shown that the sampler performs satisfactorily for $HNO_3(g)$ and SO_2.

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A Prototype Concentration Monitor for Estimating Acidic Dry Deposition

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Introduction

The assessment of ecosystem acidification and design of effective control strategies require that we monitor the deposition of major acidifying and acid neutralizing pollutants[1]. In wet deposition, pollutants are removed from the atmosphere and carried to the ground by hydrometeors. Wet deposition is far simpler to monitor than dry deposition; sampling wet deposition requires only a bucket to collect the rain or frozen precipitation. Knowledge of emissions and measurements of wet deposition indicate that wet processes typically account for the removal of about half the emissions on the regional scale. By implication, and supported by simple models, dry deposition must account for a similar amount. Unfortunately, direct verification of this inference has been impossible because of the primitive methodology for measuring dry deposition.

The difficulties of dry deposition measurement arise from our inability to distinguish pollutants deposited onto real surfaces, our inability to simulate the removal action of real surfaces, and the complexity and demanding instrumentation requirements of micrometeorological methods.[2] Measuring deposition directly to a real surface is difficult because the surface (typically vegetative) may have great quantities of the same compound in its structure and the pollutant increment is too small to be distinguished, or the pollutants may penetrate the surface and thus confound simple surface rinsing. Surrogate surfaces that avoid these problems by being inert, of different chemical composition, or non-respiratory, rarely possess the same reactivity as real vegetated surfaces. Micrometeorological methods, while having the potential of monitoring the actual flux to real surfaces, are extremely demanding of site, personnel, and equipment, usually requiring either pollutant sensors of fast response (one second or less) or highly precise chemical analysis (about 0.5-1%). While some optimism is in order for the application of micrometeorological methods, they will likely be useful mainly for site calibration and quality assurance.

Considering the importance of dry deposition and the state of technology to measure it, the National Acid Precipitation Assessment Program[1] (NAPAP) has elected to employ a method commonly called "concentration monitoring."[2,3] It is an indirect method in which concentration (C) is measured and the velocity of deposition (v_d) is estimated:

$$\text{Flux} = \overline{v_d C} \qquad (1)$$

where the product $\overline{v_d C}$ is averaged over a period of stationary conditions in the atmosphere (generally less than one hour). The term "stationary" means that atmospheric parameters are changing smoothly enough that they can be represented by average values. The deposition velocity is estimated from parameterizations based on direct measurements of flux by micrometeorological methods (and concentration) as a function of surface type, surface activity, and micrometeorology.

The first major goal of NAPAP's National Trend Network (NTN) for dry deposition is to obtain fluxes averaged over one-week intervals. If Equation 1 is applied over periods that do not have stationary conditions, then an estimate of the flux is

$$\langle \text{Flux} \rangle = \overline{v_d}\,\overline{C} \tag{2}$$

and the error in the estimate is

$$\begin{aligned} \text{Error} &= \text{Flux} - \langle \text{Flux} \rangle \\ &= (1/n) \sum_{i}^{n} (\overline{v_d C})_i - \overline{v_d}\,\overline{C} \end{aligned} \tag{3}$$

where i denotes stationary periods of uniform duration. Unfortunately, the parameters v_d and C change continuously and independently during a typical day due to the vertical mixing induced by solar radiation and horizontal winds. Since the average of a product ($\overline{v_d C}$) does not necessarily equal the product of averages ($\overline{v_d}\,\overline{C}$), there is considerable speculation as to how best to sample with the concentration monitors. The most accurate protocol would be to measure pollutant concentrations (and the meteorological variables necessary to estimate $\overline{v_d}$) over short time intervals, perhaps a few hours at most. But costs for personnel, equipment, sample analysis, and data management would be prohibitive. At the other extreme, collecting one sample over the 168 hours in a week would probably be too gross a violation of the product-of-averages constraint. Somewhere in between these two protocols lies the most cost-effective method of operating the NTN. Among the many suggestions that have been put forward, the following are receiving special attention.

Weekly Sampling. The weekly average pollutant concentration may be obtained directly from a sampler operated continuously for one week. This sampling frequency reduces analytical costs to the minimum level. However, it is unclear how to obtain the corresponding weekly average of v_d for use in Equation 1.

Daily Sampling. Some concentration monitoring networks have adopted this scheme in order to resolve the variability associated with regional-scale pollution episodes and changing weather. Such data could be combined with day-by-day evaluations of $\overline{v_d}$ to form the average deposition fluxes required. The expanded detail is at the expense of more frequent analysis.

Day/Night Sampling. It is known that v_d at night is substantially less than in daytime. Therefore, it has been suggested that much of the uncertainty associated with weekly sampling could be reduced by using two samples, one for night and the other for daytime operation, with $\overline{v_d}$ estimated accordingly.

Stability-Decoupled Sampling. The day/night variation mentioned above is largely a consequence of effects associated with atmospheric stability, which can become sufficiently great at night that dry deposition is reduced to an insignificant level (relative to daytime, unstable rates), with the possible exception of settling particles. Accordingly, sampling should perhaps be confined to periods of instability (and hence significant dry deposition) as indicated by some independent indicator of stability.

Within EPA, the Environmental Sciences Research Laboratory (ESRL) has responsibility for defining the sampling protocol for the NTN and for providing a user's guide for estimating $\overline{v_d}$ from simple meteorological observations and knowledge of the site. The Environmental Monitoring Systems Laboratory will

design the concentration monitor for the NTN, establish its operations protocol and quality assurance plan, and install the monitors. The NTN will then be operated by the U.S. Geological Survey.

Sampler Description

ESRL is developing a prototype pollutant sampler specifically for testing the various proposed sampling schemes for the "concentration monitoring" approach to dry deposition monitoring. Primary consideration has been given to the gases and fine particles that are the principal acidifiers: SO_2, HNO_3, NO_3^-, NO_2, and SO_4^{2-}. Because the uncertainty of estimating $\overline{v_d}$ is not expected to be less than ±25%, the accuracy required of concentration monitoring need be no more stringent than ±20%. In addition, many of the sampling sites will be in rural or remote areas where concentrations may be quite low; and of course, cost considerations for establishing and operating a site are very important. For these reasons, selective solid adsorption media combined with a particle filter offer the advantages of low capital cost, minimal field maintenance, ability to measure low concentrations with adequate accuracy, and analysis by the same method used for most wet deposition measurements, ion chromatography.

Shown in Figure 1, the prototype pollutant sampler is constructed of TFE Teflon, with a few short lengths of FEP Teflon tubing. It begins with a cyclone that is reported[4] to have a cutpoint of 2.1 μm for unit density particles at a flow rate of 28.3 ℓ min^{-1}. Our system is normally run with two identical 18 ℓ min^{-1} samplers following the cyclone, plus a 1 ℓ min^{-1} sweep out the bottom of the cyclone. The cyclone's inflow is 37 ℓ min^{-1}, which, by semi-empirical cyclone theory[5], reduces the cutpoint to 1.8 μm for unit density particles.

We report here the first application of a sampler based on the mass transport of a trace gas in transition flow to the reactive wall of a tube. Air at 18 ℓ min^{-1} passes through a 1-cm inside diameter Teflon tube, producing unstable, transition flow (Re = 2600). Transition flow was chosen over laminar flow because it permits sampling of more air, exhibits a high but stable transfer coefficient to the wall, and presents a laminar sublayer at the wall that impedes Brownian deposition of particles. A 3.8-cm long section of the tube is lined with a Nylon strip that reacts to collect a fraction of the $HNO_{3(g)}$ in the air stream. The air then passes through a 47-mm diameter Teflon filter (Zefluor, Membrana Corp.)[6] to remove particles, and a 47-mm diameter Nylon filter (Nylasorb, Membrana Corp.) to remove the remaining atmospheric $HNO_{3(g)}$ and any HNO_3 evaporated from NH_4NO_3 on the Teflon filter. Two ℓ min^{-1} of the air then passes through a section that is surface-coated with triethanolamine (TEA) to capture SO_2 and NO_2. Two mass flow controllers maintain the proper flowrates. The aqueous extracts of the surfaces and filters are analyzed by ion chromatography.

The sampling of HNO_3 poses a problem due to the decomposition reaction of particulate $NH_4NO_{3(s)}$:

$$NH_4NO_{3(s)} \leftrightarrow HNO_{3(g)} + NH_{3(g)}. \qquad (4)$$

A reasonable approach to sampling $HNO_{3(g)}$ without interference from the decomposition reaction is to collect a fraction on a reactive tube wall, taking advantage of the relatively high diffusive flux of a reactive gas compared to

that of particles with diameter greater than 0.001 μm. The mass flux of $HNO_{3(g)}$ to the reactive Nylon lining can be expressed in terms of a fictitious stagnant air film and turbulent core[7]. Molecular diffusion through the stagnant film controls the mass transfer to the lining, and the depletion of the trace reactive gas (HNO_3) as a function of travel distance through the tube is given by the material balance

$$-QdC(x) = F_w dA(x) \tag{5}$$

where $dC(x)$ is the change in the average concentration in the turbulent core at distance x from the inlet of the Nylon lined section, F_w is the mass flux to the lining, $dA(x)$ is the axial surface area increment, and Q is the volumetric flowrate. The radial mass flux from the turbulent core across the stagnant film to the Nylon lining is

$$F_w = D[\Delta C(r)/\Delta r]. \tag{6}$$

$$= D[(C_w - C(x)]/\ell \tag{7}$$

where C_w is the concentration of HNO_3 at the surface, and ℓ is the thickness of the fictitious stagnant film. Since HNO_3 reacts rapidly with the Nylon lining, $C_w = 0$, and Equation 5 becomes

$$-dC(x) = D[C(x)/\ell]2\pi r Q^{-1} dx \tag{8}$$

Integrating equation 8 gives the fraction of $[HNO_{3(g)}]$ penetrating the Nylon-lined section:

$$C(x)/C(0) = \exp(-2\pi r D \ell^{-1} Q^{-1} x). \tag{9}$$

The fraction of $[HNO_{3(g)}]$ deposited is

$$M = 1 - [C(x)/C(0)]$$

$$= 1 - \exp(-2\pi r D \ell^{-1} Q^{-1} x). \tag{10}$$

Thus, the fraction of $[HNO_{3(g)}]$ deposited to the Nylon lining depends on the diffusion coefficient, radius of the lined section, stagnant film thickness, flowrate, and length of the lined section. By determining M experimentally, one can use Equation 10 to estimate D/ℓ, which is known as the "transfer coefficient." The variable ℓ cannot be measured since it is fictitious, but if D is known, then an effective ℓ can be inferred.

Performance of the Sampler

In the absence of exact mass transport theory for transition flow, we experimentally determined the fractional deposition function M for $HNO_{3(g)}$. About 630 μg of nitric acid in solution (heated to aid vaporization) were injected upstream of the Nylon-lined section, and the fraction deposited determined through chemical analysis of the mass of nitrate on the Nylon lining and the Nylon filter. The results in Table I show that the Nylon lining removes a constant fraction of the $HNO_{3(g)}$ entering the Nylon-lined section at constant flowrate. The $[HNO_{3(g)}]$ fraction deposited is a function of the flowrate, decreasing about 1% for a 2% increase in flowrate. Estimates

Table I. Fraction of [HNO_3] collected by the Nylon strip.

Flowrate (ℓ min^{-1})	M, Fraction Deposited	D/ℓ (cm/sec)	ℓ (μm)	Number of Observations
15	0.100 ± 0.004	2.21 ± 0.09	540 ± 20	12
18	0.089 ± 0.004	2.34 ± 0.11	510 ± 20	10
20	0.087 ± 0.008	2.54 ± 0.25	470 ± 40	12

of D/ℓ from Equation 10 are given in Table I. These values increase as flowrate increases, indicating that the stagnant film thickness ℓ decreases, since D is constant. For a diffusion coefficient of 0.12 cm^2/sec for HNO_3, estimates of ℓ are given in Table I. The thickness of the stagnant film is sufficient to eliminate particle deposition by Brownian diffusion; for particles with diameter greater than 0.001 μm, less than 0.2% is deposited on the Nylon liner.

HNO_3/NO_3^- data are obtained from the three active surfaces in the prototype concentration monitor as follows:

If A = atmospheric HNO_3 concentration

B = atmospheric particulate NO_3^- concentration

X = mass of NO_3^- on Nylon strip

Y = mass of NO_3^- on Teflon filter

Z = mass of NO_3^- on Nylon filter

f = fraction of HNO_3 removed by Nylon strip

g = fraction of particulate NO_3^- inadvertently deposited onto the Nylon strip

h = fraction of particulate NO_3^- retained on the Teflon filter

V = volume of air sampled

k = ratio of molecular weights of NO_3^-/HNO_3 (= 62/63)

then
$$X = fkAV + gBV \quad (11)$$

$$Y = hBV(1-g) \quad (12)$$

$$Z = kAV(1-f) + BV(1-h)(1-g) \quad (13)$$

Solving for B, A, and h,

$$B = (f/(f-g))\,(X + Y + Z - X/f)\,(V)^{-1} \quad (14)$$

$$A = (X + Y + Z - BV)\,(kV)^{-1} \quad (15)$$

$$h = Y\,(1-g)^{-1}\,(BV)^{-1} \qquad (16)$$

To judge the propagation of errors resulting from uncertainties in the ion chromatographic analyses and the fractional removals (f and g, above), we ran a numerical simulation of this portion of the prototype concentration monitor over a representative range of HNO_3 and NO_3^- concentrations. For the case of the system running for 72 hours at 18 ℓ min^{-1}, with an ion chromatographic accuracy of $\pm[2.5 + 3.34(\text{sol'n concen})^{-0.843}]$% (based on typical replicate analyses), h = 0.8, f = 0.089 ±0.0036, g = 0.002 ±0.001, and a volume accuracy of ±3%, the resulting uncertainty as a percentage of concentration for a matrix of HNO_3/NO_3^- combinations is shown in Table II. While uncertainties become large at low/high and high/low HNO_3/NO_3^- concentrations, they are greatest when the corresponding concentrations are lowest, reducing the impact of the error for estimating dry deposition fluxes. In the mid-range of concentrations, the uncertainties are quite reasonable and are satisfactory for our purposes.

Table II. Uncertainty as % of concentration for HNO_3/NO_3^- determination

		$[HNO_3]$ ($\mu g\ m^{-3}$)		
		0.3	3.	20.
$[NO_3^-]$ ($\mu g\ m^{-3}$)	0.3	17/16	7/63	6/360
	3.	21/3	7/7	6/36
	20.	81/2	11/3	6/6

SO_2/NO_2 collection is by triethanolamine (TEA) coated onto substrates. Currently, we are using a cellulose fiber filter as the substrate for SO_2 collection, while substrates for NO_2 collection are under evaluation. Work to date has shown collection and recovery efficiencies of 80-100%, as well as freedom from major interferents[8]. Details of this work will be reported separately.

The field performance of the prototype concentration monitor was tested at Argonne National Laboratory (ANL) in July-August 1983. During that period we operated a modified system, in that the Teflon filter was omitted and there was no collection for NO_2. For other reasons, we ran a pair of H_2O_2 bubblers for SO_2 collection, with sulfate analysis by ion chromatography. While the sampling periods for the concentration monitor and bubblers did not always coincide, Figure 2 shows the generally good agreement between these two methods for $[SO_2]$.

HNO_3/NO_3^- data from the ANL experiment are much more limited in number and there is no other determination with which to compare. The data are

shown in Table III. The parallel HNO_3 results for each of the two runs agree fairly well. NO_3^- results are rather small concentrations, which are to be expected for summer temperatures. The low values also result in substantial relative uncertainties.

Table III. HNO_3/NO_3^- data from ANL field experiment, July-August 1983

Dates	Sampler	Total hours	$[HNO_3]$ ($\mu g\ m^{-3}$)	$[NO_3^-]$ ($\mu g\ m^{-3}$)	$[SO_4^=]$ ($\mu g\ m^{-3}$)
7/28-8/1	A	60.13	2.7 ±0.2	0.3 ±0.2	8.3 ±0.3
"	B	"	3.5 ±0.3	0.1 ±0.2	10.4 ±0.3
8/2-8/4	A	38.77	3.1 ±0.3	0.8 ±0.2	6.6 ±0.2
"	B	"	3.3 ±0.3	0.7 ±0.2	6.9 ±0.2

In a more thorough test, we recently participated in an intercomparison which included tungstic acid collection and infrared absorption methods. All investigators measured photochemically generated HNO_3 at different concentrations with and without particulate NO_3^- present. Results of this intercomparison will be reported when available[9].

Conclusions

Laboratory and limited field tests have shown that the sampler performs satisfactorily for investigating "concentration monitoring" protocols for $HNO_{3(g)}$ and SO_2. The sampler is the first reported application of unstable transition-flow mass transfer for the collection of trace atmospheric gases.

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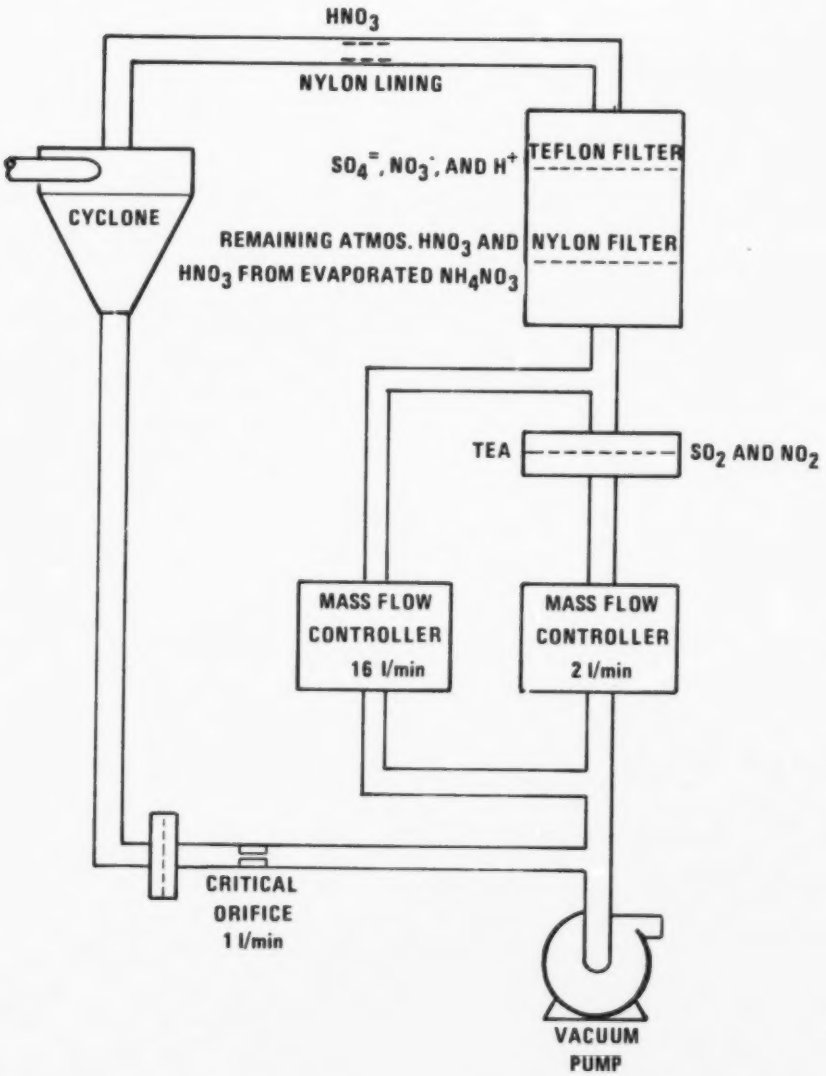

Figure 1. Prototype concentration monitor for use in establishing sampling protocol for the EPA dry deposition monitoring network.

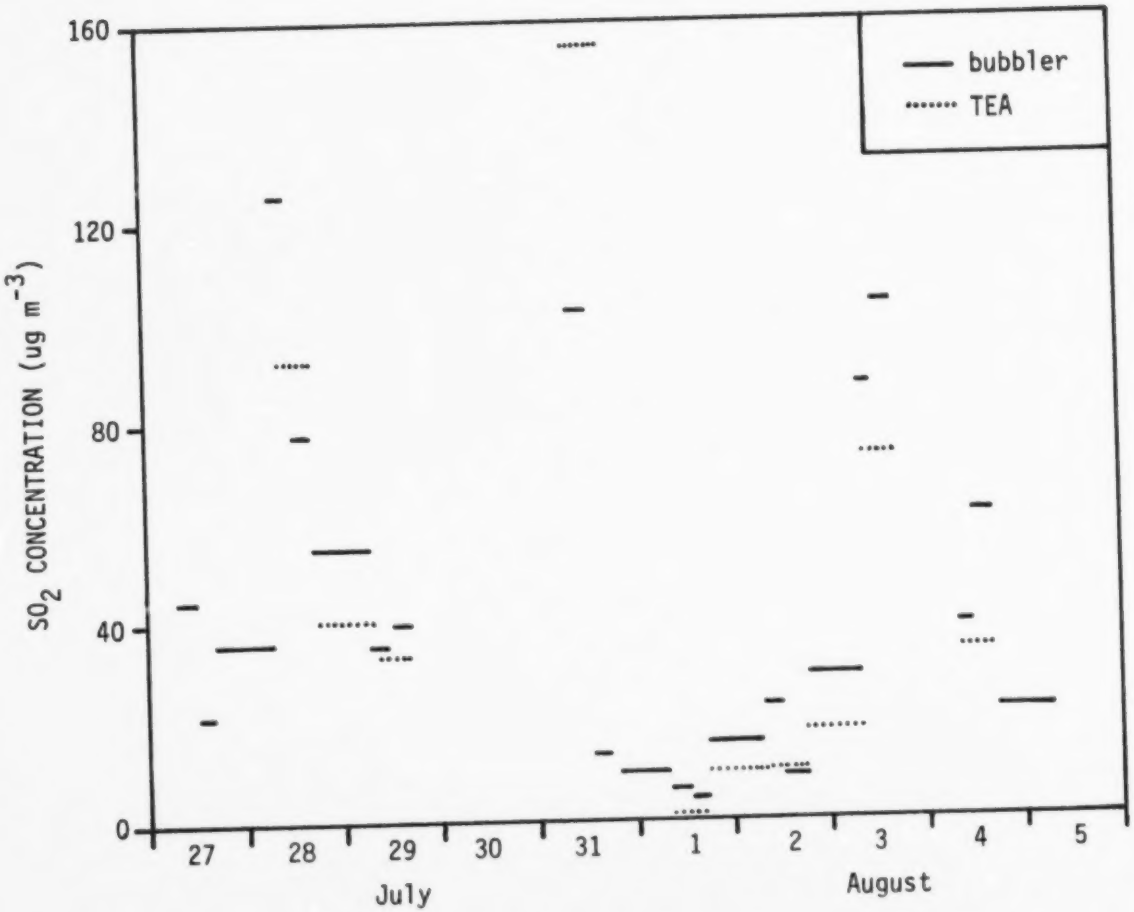

Figure 2. Sulfur dioxide concentrations measured by two methods at Argonne, Illinois, 1983.